Reactivity of Materials from Phosphate Mines

by

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February 2004

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1.0 Introduction:

Both iron and phosphate, if they occur separately in the environment, can be the source of serious environmental problems. But since they have a strong chemical affinity for each other they normally tend to keep each other in check. Since iron is one of the major drivers of acid generation many studies have explored the possibility of mixing various phosphate products, such as commercially-available fertilizer or dissolved phosphate salts, with acid generating mine wastes to reduce or even eliminate acid mine drainage (Spotts and Dolhopf, 1992; Meek, 1991; Hart *et al*., 1990; Hart & Stiller, 1991; Evangelou, 1994; Ziemkiewicz, 1990; Yanful *et al.,* 2000; Dey *et al.,* 2000). In general, the studies have concluded that while phosphate deployed in such a manner will definitely inhibit AMD, but that material and application costs make it economically impractical.

Since 1992 Boojum Research Limited has been conducting large scale field trials in which it has applied natural phosphate rock (NPR), a granular waste product of phosphate mines operated by Texas Gulf in North Carolina, to acid-generating mine wastes. These have demonstrated not only that phosphate works, but that it can provide an extremely economical solution to AMD; the trials have shown both that phosphate is effective in lower application rates as proposed by other workers, and also the phosphate is applied differently than previously suggested. It appears to be effective when it is merely scattered onto the target area - either onto tailings deposits or on waste rock, or on acid-impacted sediments of lakes - rather than mechanically mixed into the waste stream. Since the material cost of NPR is negligible the only major expenditure associated with its use, is shipping. Accordingly, laboratory tests conducted by Boojum to determine the specific chemical behaviour of the Texas Gulf North Carolina NPR, were enlarged to include NPR from mines in Ontario.

2.0 Materials and Methods

2.1 Materials

Five samples of Natural Phosphate Rock were used. The Ontario samples were obtained from the Agrium mine in Kampuskasing and the Spanish River Carbonatite deposits. The large samples were sub-sampled by the quarter method after intensive mixing. The Texasgulf samples, Code 31 and Code 48 have been used in all applications studied by Boojum Research Limited to date (Kalin et, al. 2003, Kalin and Harris, 2003). These materials have also been used in an ongoing application in a large scale Ecological Engineering project in Northern Ontario. Code 31 was used two contaminated lakes (Mud lake and Boomerang lake) in the PWP application (Precipitate With Posphate) to reduce the iron concentration in the water and reduce pH depressions due to iron oxidation.

2.2 Leach tests of the phosphate material

2.2.1 Water solubility

Slurries of ratio 1:5 and 1:10 (weight: volume) were made with distilled water, to define the initial leaching characteristics simulating rain. The slurries were allowed to stand at room temperature for one to two months and re-measured for pH, Eh, acidity, alkalinity, conductivity and phosphate concentrations. The measurements are compared for the slurry of 1:10 and 1:5 for day 0, day 30 and day 62 to assess the proportionality of the reaction, and reflecting the homogeneity/ variability of the samples. All dry samples were processed without further drying on an as received basis.

2.2.2 Sulphuric acid solubility

Slurries of 1:10 were made with 0.1N H_2SO_4. To understand the behaviour of the phosphate materials used in the sulphitic wastes, it is important to determine the sequence of the solubility, i.e. what does dissolve first or do all acid soluble elements dissolve at once. Solubility is limited by saturation of a solution. Therefore decant cycles, of short time intervals were used to reduce the effect of the reduction of dissolution due to saturation in the supernatant.

10 g of phosphate material was mixed with 100 ml of 0.1N H_2SO_4. The sample slurries were stirred vigorously with a spatula by hand for 1 minute and left to settle for 1 hr. The supernatants were decanted and analyzed for pH, Conductivity, Acidity, Alkalinity, Temperature, redox potential and phosphorous (decant cycle 0).

The decanting started with cycle one (1) with 100 ml of 0.1 N H_2SO_4 added to the remaining solids, stirred for the decant cycles with magnetic stirrer at 300 (rpm) (VARIOMAG, TELEMODULE P 20) and left to settle as described in Table 1. The slurries were then allowed to sit overnight, and the decanting was continued. With this iterative process it is expected to determine if there is a selectivity with which the elements are released from the phosphate materials tested.

Table 1: Volume Added (mL) and Reaction Time (h) for Decant Cycles 0-10

Decant Cycle	Volume	Stirring Time	Settling Time	Total Reaction Time	Cumulative Time
Sulphuric Acid					
0	100	0.02	1.0	1.02	1.02
1	100	0.5	0.5	1.00	2.02
2	100	1.7	16.0	17.7	19.68
3	100	0.5	0.5	1.00	20.68
4	200	1.0	2.0	3.00	23.68
5	100	1.0	16.4	17.4	41.05
6	100	0.5	1.5	2.00	43.05
7	100	0.5	1.0	1.50	44.55
8	200	0.42	642.8	643.2	687.7
Total	1100	6.10	681.6	687.7	687.7
Distilled Water					
9	300	1.00	2.0	3.00	3.00
10, day 0	300	21.0	2.0	23.0	26.0
10, day 62	-	-	1486.5	1486.5	1486.5
Total	600	22	1490.5	1512.5	1515.5

Spanish River Carbonatite and the material Code 31 produced decant solutions with particulates, which did not settle in the allocated settling time. Therefore 40 ml of these supernatants were centrifuged at 1000 rpm for 10 minutes to produce a decant solution, which was siphoned off the solids for acidity, alkalinity and phosphorous absorbance determination. The solids remained in the centrifuge tubes and those were stored in the refrigerator for further processing.

Once the results obtained to date are interpreted, the phosphate associated with the particulate matter in the phosphate wastes is addressed further. In the natural phosphate material, the phosphate minerals are not equally distributed. If the particle size can be related to phosphate content and to its release, then through selecting the suitable particulate fraction of the material, the costs for shipping the material for the sought application in acid generating tailings can be greatly reduced.

From each decant cycle (except 4 and 8 were 100 ml were accumulated); 50 ml of supernatant was accumulated to assess phosphate loss through precipitation reactions from the supernatant or adherence to the wall of the containers in the absence of particulates. The cumulated decant supernatants from decant cycles 0-7 were kept in fridge at 7 ^{o}C. Fifteen 15 ml of the mixed supernatant was filtered through a 0.45 µm filter paper and acidified with HNO_3 to preserve the sample for future ICP analysis. This cumulative 1.1 L could then be compared to the characteristics of a leachate obtained directly when 10 g of phosphate sample was contacted with 1 L of 0.1N H_2SO_4

When the pH values in the decant cycles with the sulphuric acid did no longer changed from the previous decant solution or remained similar to the pH value of 1.4, that of sulphuric acid, the end of the decant cycles had been reached. It is assumed, that this point represents the exhaustion of the neutralizing capacity consuming H^+. This was the case for most material after decant cycle 6 and 7 had been completed, starting with the initial solution as decant cycle (0) (see Table 3). After decant cycle 7, a further 100 ml of 0.1N H_2SO_4 was added and the slurry was stored at room temperature for 31 days. All parameters were measured again; the supernatant was removed as decant cycle 8. The beakers were covered with parafilm during the decant cycles and storage between measurements.

The solids were then allowed to air dry remaining at room temperature for a further 28 days. The slurries of Code 31 and the Spanish River samples had not been completely dry, but all others material were air-dried. After 28 days 300 ml of distilled water was added to the air dried or partially dried solids, stirred for 2 or 4 hours and settled for 3 or 23 hours respectively for two further decant cycles, 9 and 10 with distilled water. The

slurries of decant cycle 10 were let settled for another 61 days and remeasured for the 7 supernatant parameters.

No precipitates were notices in the remaining supernatants. The whole samples from decant cycles 10 are kept are kept at room temperature for phosphorous determination. The mixed samples from decant cycles 0 to 8 and samples from decant cycles were filtered and acidified for ICP-25.

The 1 L of 0.1N H_2SO_4 solution with 10 g serves to assess the rate of release of the elements of relevance. The 1 L leach was stirred for 6.1 hrs, the total stirring time observed during first phase, and left to settle for 1 hr, 2 days, 28 days, 46 days, 56 and 115 days for re-measurement. As no significant change was noticed in pH, conductivity, and redox potential between the measurements of day 46, day 56, and day 105, acidity, alkalinity and phosphorous were not determined. After day 105, the solutions were again stirred at 300 rpm for 1 hour and determined for pH, conductivity, and redox potential. Observing no effect of stirring it was decided to filter and acidify the solution for ICP-25.

The solutions were siphoned and 1 L of distilled water was added to the remained solids of each NPR separately. The solutions were stirred at 300 rpm for 1 hour and analyzed for pH, conductivity, and redox potential, temperature and acidity. The slurries were then filtered and acidified for ICP-25 and a whole samples were also spared at room temperature for phosphorous measurements. The slurries are still kept at room temperature for any further processes.

2.3 Instrumentation

A SAUTER top loading balance, with a precision of 0.01 g, was used to weigh samples. The conductivity measurements were performed using an OAKTON Con 400 series EC instrument set to mS or µS mode and temperature was recorded. The instrument adjusts the reading to 25 ^{o}C automatically. A Corning 315 pH/Ion pH meter equipped with a combination electrode also by Coring #33221 -034 was used after the pH probe was calibrated with buffers at pH 4 and 7 prior to each run of the pH determination. A Corning M103 redox instrument with an inert platinum electrode and a standard Calomel

probe was used to determine the measured redox potential (Em). Em was converted to standard redox potential at 25 ^{o}C (Eh) by using following formula:

$$Eh = Em + (241-(0.66*(\text{Sample Temperature in } ^{o}C - 25)))$$

The temperature of the solutions during the decant cycles are given in Table 2a.

Table 2: Temperature (^{o}C) Measured for Decant Cycles 0-10.

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid					
0	21.1	21.1	21.2	21.4	21.3
1	22.8	22.8	22.7	22.4	22.5
2	21.3	21.2	21.4	21.3	21.3
3	22.4	22.4	22.3	22.4	22.4
4	22.7	22.9	22.0	23.0	22.8
5	20.7	21.3	20.9	20.8	21.2
6	21.9	22.3	22.2	22.2	22.3
7	22.3	22.7	22.7	22.7	22.5
8	20.6	20.6	20.6	20.4	20.5
Distilled Water					
9	22.6	22.5	22.3	22.4	22.2
10, day 0	23.1	22.8	22.8	23.0	22.7
10, day 62	17.8	17.3	17.5	17.7	17.9

Table 3a: Eh Values Measured for Decant Cycles 0-10

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid					
0	908	663	830	813	536
1	827	675	775	692	542
2	841	732	716	635	630
3	842	564	818	843	569
4	837	690	768	760	696
5	752	607	775	702	743
6	850	846	831	806	686
7	888	839	857	811	728
8	665	712	722	693	701
Distilled Water					
9	531	512	517	461	515
10, day 0	547	517	547	506	534
10, day 62	587	532	594	570	592

Table 3b: Eh (mV) of 1 L leachate and the Cumulative supernatant

Reaction Time	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
No Decant, 10 g, 1L 0.1N H_2SO_4					
1 hr	701.3	793.5	772.7	766.9	673.0
2 days	675.7	792.2	772.4	777.2	743.9
28 days	654.7	688.8	707.8	711.7	689.7
46 days	540.0	569.0	540.0	488.0	244.0
56 days	558.3	705.4	618.4	464.0	588.6
115 days	577.5	656.4	605.6	555.4	553.4
115 days, 1hr stirring	579.2	663.5	608.4	555.0	543.0
No Decant, 10 g, 1L distilled water					
1 hr	803.8	803.8	692.8	678.2	697.5
Cumulative (DC 1-8), 1.1L 0.1N H2SO4					
31 days	671.6	725.6	711.8	719.5	701.7

Acidity and alkalinity of the samples were determined using 702 SM Titrino (Brinkmann; Metrohm). For each determination one needs 15 ml of sample. Alkalinity was only determined for the slurries made with distilled water.

Spectrophotometer (SPECTRONIC 70, BUSH & LAMB) was used for phosphorous absorbance determination using PhosVer@3 Reagent in 5 ml of decanted solutions and inverting the solution in the vial by hand for 30 seconds prior to a reaction time of 2 minutes. The colored sample is placed in the viewing tube in the spectrophotometer to measure the absorbance at 890 nm. The absorbance is converted to [P] in mg L^{-1} using a standard curve for calibration. Most of the decant solutions had to be diluted for the determination of the phosphate concentration, the correction made after the determination of the absorbance $P = \frac{Absorbance + 0.01407}{1.299834}$

Schematic of the experimental design is given at the end of document.

3.0 Results and discussion

The characteristics of the tested materials when in contact with distilled water are given in Table 4 describing the resulting slurry1:5 ratio (20 g solid: 100 ml liquid) on day 0, 30 and the results of the 1:10 ratio (10 g in 100ml), the ratio used for the nitric acid leach with the 8 decant cycles, on day 0, 30 and 62.

Table 4: Slurries 1:5 and 1:10 (solid:liquid) with distilled water day 0, day 30, day 62

NPR and Distilled Water (control)	pH			Conductivity (uS/cm)			Acidity (mg L^{-1})			Alkalinity (mg L^{-1})			Eh (mV)			Phosphorous (mg L^{-1})		
	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62	day 0	day 30	day 62
	Slurry 1:5 ratio (20 g solid: 100 ml liquid)																	
Agrium Tailings	7.44	6.92	-	121	345	-	6.6	37.8	-	14.5	65.2	-	702	407	-	1.58	0.111	-
Spanish River Carbonatite	8.73	7.23	-	102	132	-	1.5	24.7	-	47.2	57.5	-	548	416	-	0.011	0.057	-
Agrium High grade Low Fe Residium Ore	3.18	3.63	-	1200	1560	-	344	274	-	-	-	-	693	644	-	2.23	0.0801	-
Texasgulf Phosfil (Code 48)	8.53	6.70	-	174	665	-	-	54.4	-	22.9	41.3	-	562	466	-	1.42	0.0401	-
Precipitate With Phosphate, PWP (Code 31)	8.09	7.04	-	500	833	-	-	46.8	-	57.6	88.5	-	491	470	-	1.52	0.785	-
	Slurry 1:10 ratio (10 g solid: 100 ml liquid)																	
Agrium Tailings	6.49	7.45	7.73	93	281	355	14.9	32	27	5.8	48.1	45.3	454	348	359	1.06	0.07	0.10
Spanish River Carbonatite	8.79	7.26	8.15	64	118	131	8.6	15.5	8.6	38.8	72.3	57.1	386	356	353	0.011	0.01	0.01
Agrium High grade Low Fe Residium Ore	3.03	3.07	2.76	1114	1821	2880	380	339	514	-	-	-	621	659	716	1.55	0.34	0.35
Texasgulf Phosfil (Code 48)	7.44	7.53	7.52	85	465	610	7	16.2	13.2	16.9	45.2	43	499	352	530	1.00	0.05	0.08
Precipitate With Phosphate, PWP (Code 31)	7.56	7.38	7.77	288	624	681	12.7	16	14.1	39.4	64.6	53.1	430	331	513	1.20	0.88	0.74
Distilled H_2O	6.16			23			8.2			7.1			448			0.015		

The Spanish River material produced the highest pH, suggesting that the carbonate component in this material is very soluble. The Agrium High Grade Low Fe ore is acidic, with a low pH of 3.18. Both Texas gulf products and the Agrium tailings range in pH from 8.5 to 7.4 higher then the distilled water used with a pH value of 6.2.

The reproducibility of this initial reaction acceptable. The mass of the material tested is not related linearly to the elements released. This is expected, as solubility is a function of the surface area of the solid and the contact to the solution with the particulates. However to assess application rates, it is necessary to assess the reactivity in relation to weight as a practical unit. For both 10g and 20 g of material used, the trends in pH values remained the same for the slurries.

The highest conductivity was obtained in the Agrium High Grade Low Fe Ore with 1560 uS after 30 days of equilibration. None of the other material increased conductivity of the solution significantly above the distilled water value, but possibly the Code 31.

Distilled water released very little alkalinity and acidity with the exception of the Agrium High Grade Residium Low Fe Ore, which produced acidity values of 344 mg $CaCO_3$ / L. The value of acidity was the same both liquid solid ratios. The phosphate release from the

materials tested was also in the same range between 1.5 to 2.2 mg/L from 20 g or 10 g of material. The Spanish River Carbonatite material released phosphate at the detection limit. Therefore for the solubility of the material, resembling somewhat the conditions in the tailings 0.1 N sulphuric acid was used.

3.1 Hydrogen Ion consumption

Table 5a gives the *p*H values for all the samples at decant cycles 0 through 8 along with reaction times and *p*H of 0.1 N H_2SO_4. As the starting pH of the solution is pH 1.4 the effect of the material has to be evaluated based on the consumption of H^+ ions of the material. With the initial small increases after one (1) h, decant cycle zero, shortly thereafter the pH increased in pH in Code 31 and Spanish River Carbonatite . With decant cycle 8, nearly all of the neutralizing capacity of the materials was exhausted. Slight pH increases remain present in Code 48, code 31 and in the Spanish River material.

The continuation of the decanting with distilled water showed that still some acidity had remained, as the pH of the distilled water was 6.6 , the pH decreases were small, as some sulphuric acid might have remained in the solids. The highest pH slurry was noted in Code 48 in decant 9 and 10 with distilled water. It does suggest, that this material still has some neutralizing capacity remaining.

Table 5a: Supernatant *p*H over decant cycles.

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High gd Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid					
0	1.56	5.03	1.54	1.80	4.03
1	1.93	5.80	1.79	2.58	3.63
2	2.00	7.29	2.01	3.24	3.62
3	1.63	5.32	1.64	1.50	3.29
4	1.54	6.27	1.70	1.62	3.23
5	1.73	4.25	1.68	2.25	3.39
6	1.51	1.87	1.49	1.55	3.29
7	1.59	1.79	1.44	1.49	3.26
8	1.67	2.66	1.77	3.12	2.74
Distilled Water					
9	4.19	3.96	3.23	5.72	3.42
10, day 0	4.72	4.09	4.07	5.73	4.16
10, day 62	3.82	3.98	2.82	6.09	3.65

In Table 5b the H+ ion consumption is calculated for decant cycles 0 to 8 by converting the pH unit to [H+]. The *p*H is converted into hydrogen ion consumed, H^+ (mol) using relationship; $H^+ = (10)^{-pH}$ mol. The H^+ consumed by the phosphate materials during each decant cycle were then calculated by subtracting sample H^+ from 0.1N H_2SO_4 H^+.

This difference of consumption in moles [H+] and is also given as the value of pH unit change. The Agrium High Grade Low Fe Residum Ore appears to have been exhausted, no longer able to release H+ with the 8th decant cycle, whereas in all other material some H+ consumption does remain.

Table 5b: Hydrogen Ions consumed and pH unit changes in sulphuric acid leach cycles

Decant Cycle	Agrium Tailings		Spanish River Carbonatite		Agrium High grade Low Fe Residium Ore		Texasgulf Phosfil (Code 48)		Precipitate With Phosphate, PWP (Code 31)	
	[H+] consumed mol	Unit change	[H+] consumed mol	Unit change	[H+] consumed mol	Unit change	[H+] consumed mol	Unit change	[H+] consumed mol	Unit change
0	1.20E-02	0.16	3.99E-02	3.63	1.08E-02	0.14	2.42E-02	0.40	3.98E-02	2.63
1	2.81E-02	0.53	3.99E-02	4.40	2.36E-02	0.39	3.73E-02	1.18	3.97E-02	2.23
2	2.99E-02	0.60	3.99E-02	5.89	3.00E-02	0.61	3.93E-02	1.84	3.97E-02	2.22
3	1.62E-02	0.23	3.99E-02	3.92	1.68E-02	0.24	7.91E-03	0.10	3.94E-02	1.89
4	1.09E-02	0.14	3.99E-02	4.88	2.01E-02	0.31	1.59E-02	0.22	3.93E-02	1.83
5	2.13E-02	0.33	3.98E-02	2.85	1.89E-02	0.28	3.42E-02	0.85	3.95E-02	2.00
6	8.64E-03	0.11	2.64E-02	0.47	7.84E-03	0.10	1.15E-02	0.15	3.94E-02	1.89
7	1.39E-02	0.19	2.36E-02	0.39	3.93E-03	0.04	7.84E-03	0.10	3.94E-02	1.86
8	1.85E-02	0.27	3.77E-02	1.26	2.29E-02	0.37	3.91E-02	1.72	3.81E-02	1.34

Table 5c represents the rate of [H+] consumption per g of material per reaction time in each decant cycle. The reaction rate is reduced by one order of magnitude when the material sits over night and for decant cycle 8 with the longest contact time, the reaction rate is the lowest. These reaction rates suggest that the release is related to the contact of the particulates with the sulphuric acid. Only two solutions have a reasonable pH increase, Code 31 and Spanish River Carbonatite. This suggests that the consumption of H^+ ions is exhausted when the consumption rate is reduced to a rate ranging between 2 to 4×10^{-7} mol/g/min at decant cycle 5. For most materials the rate of H^+ ion consumption is becoming low with the remaining cycles and not much more can be extracted from the 10 g of material used in the tests.

Table 5c: Hydrogen ion consumption rate in mol/ gram of sample/ min

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
	[H+] consumed mol/g/min	[H+] consumed mol/g/min	[H+] consumed mol/g/min	[H+] consumed mol/g/min	[H+] consumed mol/g/min
0	1.97E-06	6.54E-06	1.77E-06	3.96E-06	6.53E-06
1	4.68E-06	6.65E-06	3.93E-06	6.21E-06	6.61E-06
2	2.82E-07	3.76E-07	2.83E-07	3.71E-07	3.74E-07
3	2.70E-06	6.65E-06	2.81E-06	1.32E-06	6.56E-06
4	1.21E-06	4.43E-06	2.24E-06	1.76E-06	4.37E-06
5	2.15E-07	4.02E-07	1.90E-07	3.45E-07	3.98E-07
6	7.20E-07	2.20E-06	6.53E-07	9.55E-07	3.28E-06
7	1.54E-06	2.63E-06	4.36E-07	8.71E-07	4.37E-06
8	9.60E-09	1.95E-08	1.19E-08	2.03E-08	1.97E-08

It also warrants to check if the solution becomes saturated, as the volume of acid used in the decant cycles might be too small in relation to the amount of which could dissolve.

To assess the saturation 10 g of the material was added to 1 L of 0.1 N sulphuric acid directly. The resultant leach solution is measured for the same parameters. These result of the 1 L leach is presented together with the characteristics of the cumulated decant cycles (Table 5d). Comparing these pH values of the two solutions, they are similar to that of the sulphuric acid with pH 1.4. During storage, the cumulative supernatant from the decant cycles remain the same.

Table 5d: pH of 1 L supernatant and cumulative

Reaction Time	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
No Decant, 10 g, 1L 0.1N H_2SO_4					
1 hr	1.57	1.64	1.43	1.46	2.08
2 days	1.68	1.93	1.53	1.59	2.32
28 days	1.77	2.74	1.79	1.87	3.05
46 days	1.69	2.99	1.81	1.98	3.01
56 days	1.76	3.03	1.83	2.09	3.10
115 days	1.83	3.36	1.87	2.41	3.11
115 days, 1hr stirring	1.99	3.45	1.95	2.59	3.22
No Decant, 10 g, 1L distilled water					
1 hr	3.40	4.22	3.35	4.08	3.65
Cumulative (DC 1-8), 1.1L 0.1N H_2SO_4					
31 days	1.56	2.48	2.0	1.73	3.13

3.2 Electrical Conductivity

Generally when elements dissolve into distilled water it is expected that the electrical conductivity (EC) with increase. The reverse takes place when elements are released to sulphuric acid. The available sulphate reacts with cations released, resulting in a decrease of EC. The initial electrical conductivity values of the acid is 37,800 uS/cm. For decant cycles 9 and 10 the EC of the distilled water was 23 uS/cm.

In Table 6a the EC values are given for the supernatants of the decant cycles. When the slurries have more time to react, the EC values decrease more significantly, as noted for decant cycle 2, and 5, where the slurries were reacting over night. The lowest values for the sulphuric acid decants are reported for decant cycle 8. In the following distilled water decant cycles, a large reduction is taking place, one order of magnitude lower, signaling the end of the release of the elements. It is reasonable to conclude, that for most materials the release of elements has been exhausted.

The differences between sulphuric acid EC and those with the material are given as decreases in Table 6b. The code 48 and the Spanish River Carbonatite had the highest decrease or release of cations, reflected in the largest reductions of the EC values. On the other hand, Agrium tailings appears not to have a large amount of sulphuric acid dissolvable cations, with only minor decreases in EC values. With time however the difference in EC decrease. Code 31 the fine ground phosphate, with the high surface area has more cation available as the EC values from decant cycle 0 to 7 hardly changed.

Table 6a: Measured electrical conductivity for various decant cycles

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid					
0	19110	5250	32300	13170	6980
1	10820	3690	13800	6030	5500
2	8300	2730	9360	4040	4160
3	18020	3230	17110	31900	4850
4	17680	2710	12160	14030	4490
5	12160	2750	14710	6590	4300
6	19090	10020	31800	18750	4510
7	16550	11220	33000	31200	6700
8	7670	2980	6350	2650	3180
Distilled Water					
9	950	1693	1117	1435	1883
10, day 0	938	1704	1010	740	1742
10, day 62	1294	1752	1960	1775	1800

Table 6b: Conductivity reductions during decant cycles

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
0	-18690	-32550	-5500	-24630	-30820
1	-26980	-34110	-24000	-31770	-32300
2	-29500	-35070	-28440	-33760	-33640
3	-19780	-34570	-20690	-5900	-32950
4	-20120	-35090	-25640	-23770	-33310
5	-25640	-35050	-23090	-31210	-33500
6	-18710	-27780	-6000	-19050	-33290
7	-21250	-26580	-4800	-6600	-31100
8	-30130	-34820	-31450	-35150	-34620

A significant reduction in EC however takes place during decant cycle 8 reducing the conductivity by 1 order of magnitude for all samples (Table 6a), and this is also the case in the 1 L direct leaching (Table 6c) . This reflects the slower reaction , where the salts form, and gradually decrease the EC of the solution. The range of EC noted after 31 days in the cumulative and at 46 days in the 1 L solutions is very similar.

These observations suggest that release of elements takes place initially rapidly, reflecting first order kinetics, which is followed by a gradual release and formation of salts, such as calcium sulphate thereafter. The aim of the experiment is to assess in some

systematic way the reactions in the tailings pore water. Both dissolution of elements and precipitation of reactants take place simultaneously or in sequence, both altering the solution and thus the conditions for dissolution from the solid to the liquid. The similarity of the conductivity of the 1 L leach, the cumulative decant EC and the decant cycle 8 EC values do indicate that the experiment might need to be continued after detailed evaluation by Dr. Meinrath.

Table 6c: Conductivity changes

Reaction Time	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
No Decant, 10 g, 1L 0.1N H_2SO_4					
1 hr	10980	8200	12200	11220	5140
2 days	8500	5220	10470	9170	3760
28 days	6860	2560	6900	5920	2960
46 days	6730	2310	6430	4960	2980
56 days	6881	2330	6510	4630	3060
115 days	7500	2230	6650	3550	3130
115 days, 1hr stirring	7260	2140	6580	3500	3110
No Decant, 10 g, 1L distilled water					
1 hr	1135	1132	1212	1427	1875
Cumulative (DC 1-8), 1.1L 0.1N H2SO4					
31 days	10880	3000	10780	8200	3070

3.3 Metal Acidity

Table 7a presents the measured acidity (mg L^{-1}) for the samples at decant cycles 0 through 8. Acidity is the parameter, which will describe both the consumption of hydrogen ions along with the interaction of the dissolved elements from the phosphate materials as the pH is raised by the titration. In Table 7a the acidities are given for the 8 decant cycles. The immediate neutralization capacity of the Spanish River material is evident , followed by code 31 code 48 and the smallest reduction from the initial acidity of the sulphuric acid used with 6203 mg $CaCO_3$ equivalent / l are the Agrium mine materials. The release of the alkalinity, to reduce the acidity in the Texas gulf materials , Code 48 is gradual, but remains very consistent for code 31 throughout all decant cycles, and is rapid for the Spanish River material. This characteristic relevant to the longevity of inhibition or acid reduction observed in the use of the Texas gulf material on tailings and in waste rock, as the acid generation process is a gradual one, and through the anticipated

precipitation of Fe^{3+} which takes place above pH 3 , the acid generating process rate is reduced.

The acidity of distilled water used for decant cycles 9 and 10 is negligible, with 7 mg/l and hence the last two decant cycles for most of the materials indicate low dissolution, with the exception of the Code 31 material.

Table 7a: Acidity measured (mg L^{-1}) for DC 0-10

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid					
0	4945	487	4943	3378	2719
1	4250	229	4652	2248	2723
2	3634	73	3795	1814	2279
3	4848	417	4809	4494	2979
4	4751	113	4437	3894	2805
5	4251	218	4384	2863	2722
6	4867	2364	4778	4477	2872
7	4864	4504	4759	4537	2818
8	3993	1236	3795	1872	2928
Distilled Water					
9	50.2	99.6	157.9	44.5	583.3
10, day 0	36.4	54.4	45.9	45.6	176.4
10, day 62	45.2	68.5	142.3	14.7	195.9

In Figure 1 to 3 the titration curves of decant cycle 1, 8 and the 1 L leach are presented along with that of the 0.1 N sulphuric acid. From the Spanish River Carbonatite material very little is material released, as the curve has very small plateaus, representing a very steep line. Agrium tailings and High Grade Low Fe Ore are similar, having a plateau around in the low pH range of 1 to 2.5 and a second distinct area of precipitation around pH 5 to 8, where a second group of elements precipitate from the solution during titration as the pH increases. For Code 31 and Code 48 the curves have also two plateaus, except the one in the low pH range is absent or very small.

Figure 1: Titration Curves, Decant Cycle 1

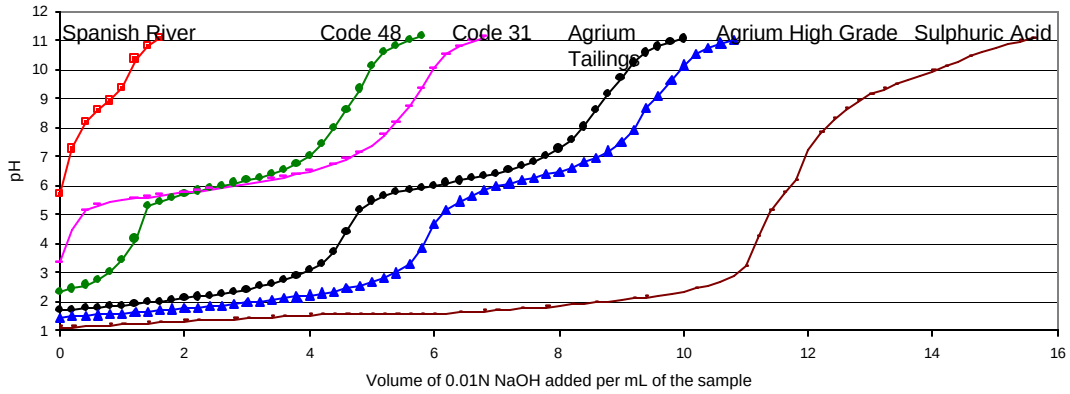


Figure 2: Titration Curves, Decant Cycle 8

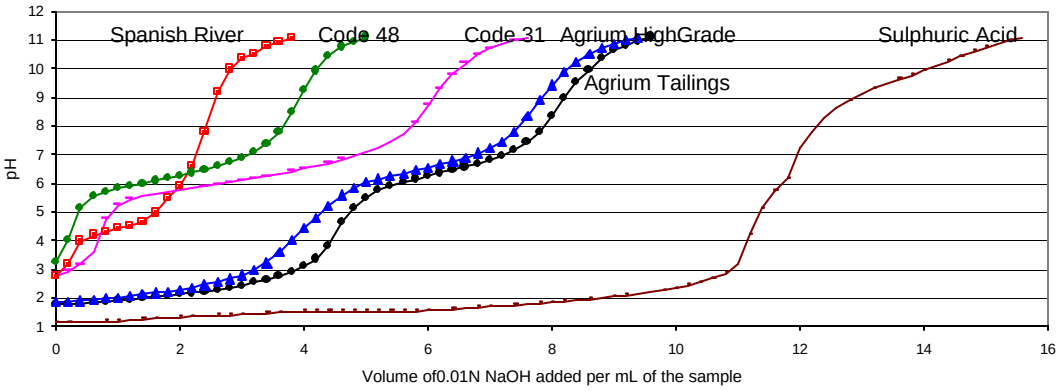
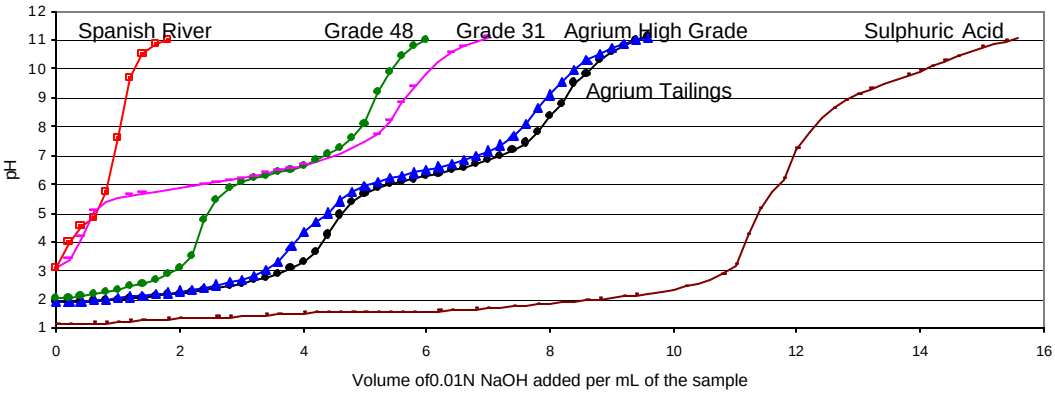


Figure 3: Titration Curves, 1L, 10g, 46 days



The differences between the decant cycles and the 1 L leach solutions are small. A shift in the amount of elements in the solution, which is available to precipitate, is noted. The Agrium tailings and the High Grade low Fe Ore curves are becoming more similar. Code 48 and 31 differentiate themselves more are after 8 decant particularly with elements, which introduce a plateau in the titration curve around pH 7, as Code 31 has a more extensive plateau than does Code 48. However the plateau between pH 1 and 2 is shorter for both Codes, suggesting that some Al and Fe which was initially in solution has precipitated or these elements are depleted from the solid material. This is not the case for the materials from the Agrium material as even after decant cycle 8 and in the 1 L solutions this plateau exists. The Spanish River material does start to release at decant 8 some elements into the supernatant, but only around pH 4 these elements start to precipitate.

As a first approximation , the materials from the Agrium mine, both ore and tailings are very different from the phosphate materials from the North Carolina deposit. The contribution of a reduction in acidity of the sulphuric acid originates from the dissolution of different group of elements. It is likely that these elements are Fe^{3+} and Al^{3+} , but this needs to be confirmed with further analysis. The Spanish River material has lot of neutralizing capacity, as it contains 65 % Calcite as $CaCO_3$ which increased the pH and subsequently no other elements are released. This certainly does not make suitable for the intended application of acid mine drainage in sulphitic waste material, as it essentially functions like limestone. Phosphate does not get released in a elevated pH environment and thus is not available to precipitate the Fe^{3+} , a reaction that is considered the most important one to take place in all phosphate applications to sulphitic mining wastes.

In Table 7b the net reduction in acidity are given by subtracting the acidity value of the sulphuric acid for the decant cycles. Table 7c gives the rate of acidity reduction. These data reflect clearly the steady release neutralizing capacity of the Texas gulf materials throughout the decant cycles of the Code 31 material. The Agirum tailings, resembling most the Code 48. The fast reaction of the Spanish River Carbonatite is evident. In decant cycle 8, it appears that as the material sits, no further reaction takes place for all materials.

Table 7b: The net acidity reduction (mg/L).

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
0	-1255	-5713	-1257	-2822	-3481
1	-1950	-5971	-1548	-3952	-3478
2	-2566	-6127	-2405	-4386	-3921
3	-1352	-5783	-1391	-1706	-3221
4	-1449	-6088	-1763	-2307	-3395
5	-1949	-5982	-1816	-3337	-3478
6	-1333	-3836	-1422	-1724	-3328
7	-1337	-1696	-1441	-1663	-3382
8	-2207	-4964	-2406	-4328	-3272

Table 7c: Rate of Acidity change (mg/g/min).

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
0	-0.21	-0.94	-0.21	-0.46	-0.57
1	-0.33	-1.00	-0.26	-0.66	-0.58
2	-0.02	-0.06	-0.02	-0.04	-0.04
3	-0.23	-0.96	-0.23	-0.28	-0.54
4	-0.16	-0.68	-0.20	-0.26	-0.38
5	-0.02	-0.06	-0.02	-0.03	-0.04
6	-0.11	-0.32	-0.12	-0.14	-0.28
7	-0.15	-0.19	-0.16	-0.18	-0.38
8	-0.001	-0.003	-0.001	-0.002	-0.002

In Table 7d the acidities of the 1 L leaching of 10 g of material is presented compared to the cumulated decanted solutions stored for 31 days. These acidities reflect those of the decant cycles very closely for all materials, with the exception of the Spanish River Carbonatite, were the reductions appear to be higher in the 1 L with lower readings as in the decant cycles. This is most likely due to the gradual precipitation of calcium-sulphate from the solution.

Table 7d: Acidity (mg/L) of the supernatants

Reaction Time	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
No Decant, 10 g, 1L 0.1N H_2SO_4					
1 hr	4690	2366	4807	3971	3521
2 days	4427	1382	4561	3524	2193
28 days	4036	596	3973	2704	2771
46 days	3987	533	3839	2519	2716
No Decant, 10 g, 1L distilled water					
1 hr	63.7	22.2	87.5	50.9	447.9
Cumulative (DC 1-8), 1.1L 0.1N H2SO4					
31 days	4370	646	4316	3132	2643

3.4 Phosphorous concentrations

Table 8 presents the measured phosphorous (mg L^{-1}) in the decant cycles 1 to 8. The lowest release of phosphate is associated with the Spanish River Carbonatite. This material only started to release phosphate after decant cycle 4. The amount generated during the subsequent decant cycles is minimal compared to that of other rocks which generated a significant phosphorous. The phosphate release of Code 31 is very consistent with the intended application in sulphitic wastes, releasing a steady amount with each decant cycle.

The sulphuric acid used in this test procedure contained a small amount of phosphorus , namely 0.38 mg/L, which when considered (Table 8b) indicates that not phosphate was released from the Spanish River Carbonatite. For the other decant cycles, the amount of phosphate in the sulphuric acid is not noted. The materials from the Agirum mine are releasing similar amounts of phosphate as the Texas gulf material.

Table 8a: [P] (mg L^{-1}) over decant cycles

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
Sulphuric Acid					
0	58	0.059	118	189	473
1	358	0.189	324	341	659
2	582	0.011	613	502	686
3	255	0.18	321	127	713
4	269	0.41	563	273	767
5	509	1.03	413	536	629
6	223	1.29	215	184	890
7	232	1.5	163	152	706
8	536	2.14	613	544	949
Distilled Water					
9	2.7	0.03	20	3.1	107
10, day 0	1.8	0.03	4.6	2.6	30
10, day 62	2.7	0.01	3.6	0.52	8.1

Table 8b: Phosphorus change (mg/L) for various decant cycles

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
0	57	-0.32	118	189	473
1	358	-0.19	324	341	659
2	582	-0.37	613	501	686
3	255	-0.20	320	126	713
4	269	0.03	563	272	767
5	509	0.65	413	536	628
6	222	0.91	215	184	890
7	232	1.12	163	151	705
8	536	1.76	613	544	949

The rate of phosphorus release is calculated for the material in Table 8c. Both the Agrium materials release phosphate at a rate, similar to the Code 48 material. Code 31 both with respect to acidity reduction and phosphate release shows the best performance.

Table 8c: Rate of Phosphorus change (mg/g/min) for various decant cycles

Decant Cycle	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
0	0.009	0.000	0.019	0.031	0.078
1	0.060	0.000	0.054	0.057	0.110
2	0.005	0.000	0.006	0.005	0.006
3	0.043	0.000	0.053	0.021	0.119
4	0.030	0.000	0.063	0.030	0.085
5	0.005	0.000	0.004	0.005	0.006
6	0.019	0.000	0.018	0.015	0.074
7	0.026	0.000	0.018	0.017	0.078
8	0.000	0.000	0.000	0.000	0.000

The results of the cumulative leach solution compared to the 1L 10 g leach are given in Table 8d. It is interested to note, that in the one leach, the unstirred solution the phosphate decreased in the Code 31. This is not the case for the cumulative solution. Although it might be suspected that this is due to precipitation, which takes place, this can not be suspected, as the estimated concentrations and the measured concentrations of the cumulative solution are in good agreement, for all but the Spanish River solution (See Table 8e). It may be possible that the phosphate is adsorbing onto the surfaces, or that the measurement is in error.

Table 8d: Phosphate concentration in cumulative and 1L solution

Reaction Time	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
No Decant, 10 g, 1L 0.1N H_2SO_4					
1 hr	297.8	12.3	243.9	168.9	605.5
2 days	474.7	20.7	378.5	474.7	703.2
28 days	564.7	7.27	603.2	364.7	734.0
46 days	584.0	5.18	626.3	403.2	480.1
No Decant, 10 g, 1L distilled water					
1 hr	4.86	0.011	9.67	9.09	11.02
Cumulative (DC 1-8), 1.1L 0.1N H2SO4					
31 days	368.9	4.90	410.9	341.6	774.7

3.5 Particulates, precipitates and solid composition

Precipitate formation or the effect of suspended particulates in the stored decant solution is tested with additional measurement after 57 to 58 days or storage. The solution was first measured prior to mixing the settled particulates, determining pH and the phosphate concentration. The fine particulate of the Spanish River Carbonatite did not settle during the regular settling time of the decant cycles. Thus the solutions were always centrifuged, whereas the Code 48 did have no particulates producing a clear supernatant. To ascertain, that indeed the distribution of the particulates and the segregation of the material either with or without centrifugation did not affect the solution chemistry and most importantly the dissolution of phosphate, a comparison was made using decant cycle 2 from the first day and after storage of 57 or 58 days. From the results it is evident, that these experimental procedures did not influence the dissolution of phosphate. (Table 8f).

Table 8e: Particulate formation during storage

Parameters	Decant Cycles	Spanish River Carbonatite			Texasgulf Phosfil (Code 48)		
		Centrifuged		Non Centrifuged	Centrifuged	Non Centrifuged	
		Day 1	Day 58	Day 58	Day 58	Day 1	Day 58
pH	2	7.3	7.7	NA	3.0	3.2	NA
	8*	2.7	2.8	2.8	3.1	3.1	3.1
[P], mg/L	2	0.01	0.01	0.01	490	502	486
	8*	2.14	2.10	2.16	556	544	563

* The difference between the first and the last measurements for DC 8 was 57 days
NA: Not sufficient sample available for measurement

To assess how much of the total phosphate content was released with the experiment to date, the materials were ground in a hand mortar and submitted to an analytical laboratory to ICP analysis. The digestions of the samples is a nitric/perchloric digest, thus the phosphate will become available, but not the silica. In Table 9 the elemental composition is given for the materials tested. For the estimate of the amount of solids released, the phosphate concentrations in the solids are used. For the estimated phosphate release, the concentrations in the solids are given for 10 g or sample used, and the mass is accumulated according to the amount (50 ml) of supernatant cumulated (Table 8f). Although the phosphate release from the Agrium materials is certainly in the same range as that of those materials from Texas gulf, whereas the Spanish River material does has a

very stable phosphate, likely highly crystalline. The good agreement between the measured and the calculated cumulative solution, also indicated, that precipitation does not seem to take place.

Table 8f: Estimated phosphate release from solids

Parameters	Agrium Tailings	Spanish River Carbonatite	Agrium High grade Low Fe Residium Ore	Texasgulf Phosfil (Code 48)	Precipitate With Phosphate, PWP (Code 31)
P content, mg/10 g	1120	141	938	900	1330
% dissolved	34	0.7	48	39	61
Theoritical, [P], mg/L in cumulative supernatant	348	0.85	411	320	740
Measured [P], mg/L	369	4.9	411	342	775

In Table 9 the elemental composition of all materials tested is given. The major elements are given in percent the minor elements as ug/g. For the material used in the phosphate tests for code 31 and 48 several individual analysis are listed, as for the Ontario materials only one analysis has been carried out. The Code 48 a and 48b analysis was exposed on Cupper Zinc tailings, to weather for 4 years, hence the material has higher values of Cu and Zn, then the back ground value 3 to 10 ug/g or 63 to 341 ug/g for representing the range for both Texas gulf material.

The reason the analysis are included is to highlight the point, that in the rain, the phosphate is not released in the absence of acid, as concentrations of phosphate have reduced minimally. Analysis is also presented for the grey and white gravel pieces, constituting the Code 48 formulation. The difference in the elemental composition of the two gravel pieces is not very large, possibly for P where the white gravel contained 6.1 % and the grey gravel 10 %. The composition of the Ontario materials however differs from the Texas gulf product, with respect to the iron content, considerably higher than that from Texas gulf. This may be a reason for caution for its use, but it depends on the relative amount of iron present in the mining waste material to be treated.

From the minor elements, the Texas gulf material differentiates itself also from that material in Ontario, with the presence of higher barium, manganese and titanium

concentrations. However these differences are not relevant, given that the application rates would make those elements likely undetectable after the use of these materials.

Table 9: Concentration of Elements in Phosphate Samples

Elements	Phosphate Samples											
	Code 31	Code 30	Code 30	Code 31	Code 48	Code 48a	Code 48b	Code 48 (White)	Code 48 (Gray)	Agrium Tailings	Spanish River	Agrium High Grade
Major Elemets (%)												
Al	0.21	0.20	0.20	0.24	0.29	0.55	0.97	0.22	0.41	0.28	1.48	1.38
Ca	31.1	33.1	33.4	35.2	32.3	31.1	17.8	30.7	27.6	27.5	22.2	25.6
Fe	0.33	0.32	0.36	0.39	0.49	0.67	12.7	0.42	0.78	12.50	4.34	4.43
K	0.08	0.08	0.11	0.11	0.15	0.16	0.14	0.11	0.19	0.02	0.77	0.01
Mg	0.31	0.32	0.28	0.32	0.48	0.32	0.21	0.39	0.26	0.09	1.05	0.16
Na	0.69	0.76	0.75	0.78	0.55	0.58	0.32	0.43	0.69	0.15	0.34	0.13
P	12.1	12.8	12.3	13.3	7.96	8.92	9.04	6.13	9.97	11.2	1.41	9.38
S	1.06	1.03	1.21	1.22	0.95	1.22	0.00	0.65	1.13	0.20	0.05	2.45
Sr	0.23	0.26	0.24	0.26	0.20	0.19	0.10	0.17	0.20	0.28	0.30	0.33
Minor Elements (ug/g)												
Ba	38	41	38	46	31	34	33.7	28.8	46	260	400	390
B	872	824	851	842	310	364	32.6	94.8	1030	360	40	82
Cd	39	38	44	43	2	5	22.1	5.9	8.7	8.2	0.9	2.5
Co	-1	-1	-1	-1	-1	-1	-0.3	0.6	1.2	83	12	140
Cr	117	128	125	139	53	58	90.6	52.7	81.2	19	-0.5	98
Cu	7	8	9	10	3	99	365	7.2	9.7	17	18	64
Mn	13	12	41	20	17	74	121	12.2	10.9	1780	880	610
Ni	13	15	17	16	8	13	4.1	11.1	19.5	34	0.9	94
Pb	-3	-3	-3	-3	-3	-3	-1	-1	-1	35	4	25
Ti	52	12	35	33	44	47	93.5	60.5	88.3	400	1880	100
V	18	20	20	22	19	20	29.4	18	24.5	350	51	380
Zn	307	308	341	337	63	1320	2330	73.1	97.1	260	59	340

4.0 Conclusions

To come after Dr. Meinrath evaluation

5.0 References

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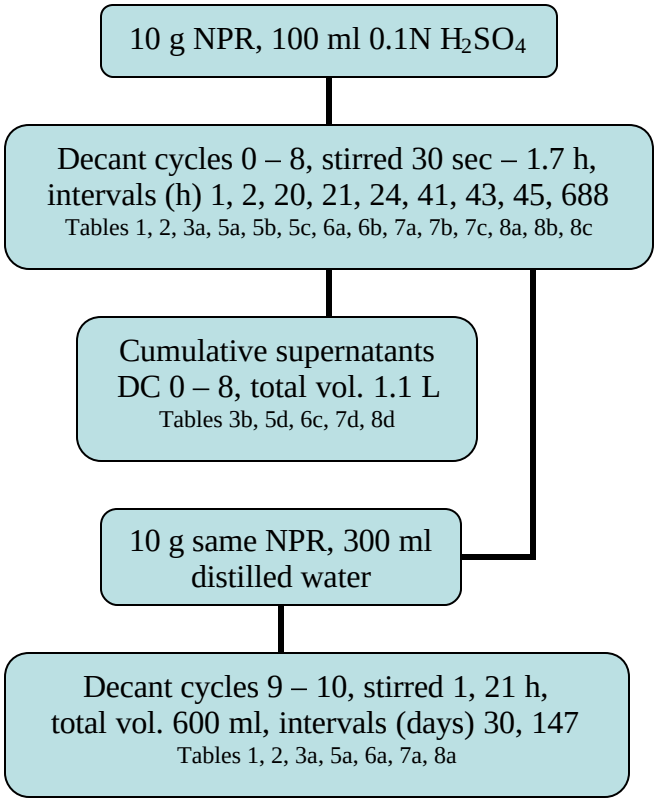
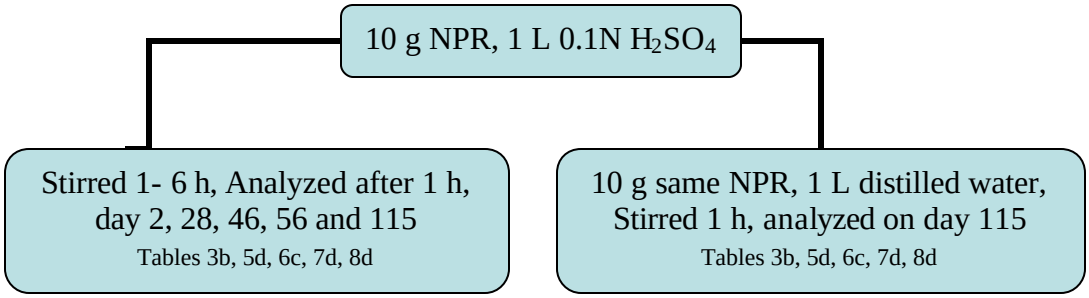
Schematic 1: Experimental design

1a. First Run: Leaching NPR with 100 ml 0.1 N H_2SO_4 and 300 ml distilled water



1b. Second Run: Leaching NPR with 1 L 0.1 N H_2SO_4 and 1 L distilled water



1c. Rain simulation: Leaching NPR with 100 ml distilled water